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| (21) International Application Number: PCT/US96/15940 (22) International Filing Date: 4 October 1996 (04.10.96) (30) Priority Data: 08/540,395 6 October 1995 (06.10.95) US (71) Applicant: CABOT CORPORATION [US/US]; 75 State Street, Boston, MA 02109-1806 (US). (72) Inventors: CULP, David, E.; 255 East Washington Street, Arcola, IL 61910 (US). LAUFHUTTE, Rudiger; 765E County Road 1050N, Tuscola, IL 61953 (US). LUCARELLI, Michael, A.; 7 McGinnis Place, Mattoon, IL 61938 (US). LIN, Bob, Tse-Weng; 2707 Woodbridge Road, Champaign, IL 61821 (US). LEMAN, Gregory, W.; Rheinstrasse 62f, D-79639 Grenzach-Wyhlen (DE). LEHMANN, Helmut, T.; Gustav-Adolf-Strasse 20, D-63452 Hanau (DE). (74) Agent: LANDO, Michelle, B.; Cabot Corporation, 157 Concord Road, P.O. Box 7001, Billerica, MA 01821-7001 (US). | | (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| (54) Title: AQUEOUS THIXOTROPES FOR WATERBORNE SYSTEMS (57) Abstract <p>Aqueous thixotropes for waterborne systems are disclosed including an aqueous dispersion of fumed silica and a waterborne resin. The waterborne resin is selected from the group consisting of alkyd, acrylic, polyester, polyether, silicate, urethane, epoxy, formaldehyde, vinyl, and mixtures thereof. The fumed silica has a surface area between about 85 m²/g and about 410 m²/g, and is present in the system in an amount between about 0.5 and about 10.0 % by weight, of total resin solids.</p> | | |

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TITLE**AQUEOUS THIXOTROPES FOR WATERBORNE SYSTEMS**BACKGROUND OF THE INVENTION1. Field of Invention:

5 The present invention relates to aqueous thixotropes for waterborne systems and, more particularly, to aqueous dispersions of fumed silica for use as effective thixotropes and rheology control agents in waterborne systems.

2. Description of the Related Art:

Both hydrophilic and hydrophobic fumed silicas are widely used in the coating industry
10 to improve rheology, for flow control and storage stability, as well as serve as an anti-settling agent for pigments and fillers. The production of hydrophilic fumed silica is a well known process. Grades vary in particle and aggregate size. Hydrophobic silica can be produced by treating a fumed silica with a suitable agent which will vary depending on the desired degree of hydrophobicity and other characteristics. Such treating agents include, for example,
15 polydimethylsiloxane oils of various molecular weights, dimethyldichlorosilane, trimethoxyoctylsilane, disilazanes, such as hexamethyldisilazane (HMDZ), and mixtures thereof.

In aqueous systems, which include both emulsions and water reducible vehicles, untreated (hydrophilic) silicas are typically not effective because of the large concentrations of silica that are necessary to realize the desired thickening. However, methods exist for increasing the
20 thickening capability of a given concentration of silica by using certain substances as additives to modify the nature of the system. For example, in systems that are not readily responsive to fumed silica because of inherent chemical properties, the correct additive can often facilitate efficient viscosity and thixotropic control. For example, in highly hydrogen-bonding liquids, the additives that are typically most useful in improving the thickening and thixotropic efficiency of
25 fumed silica are cationic surfactants. The surfactants modify and partially impede the interaction between fumed silica and the solvent, thereby allowing the fumed silica network structure to

develop, thus resulting in improved viscosity, thixotropy, and suspending properties. In non-hydrogen-bonding liquids, the additives which prove most useful are short chain molecules with more than one functional group capable of hydrogen bonding, such as glycols. These molecules act as bridging compounds between the surface hydroxyls of fumed silica aggregates, which form chains consisting of alternating silica aggregates and organic molecules. Such systems require the separate addition of certain additives to untreated silica dispersions.

As environmental awareness increases, manufacturers face increased pressure to replace conventional solvent based systems. As a result, aqueous systems are increasingly used in many applications such as automotive and industrial coatings, paints, inks, adhesives, and the like. While hydrophilic and hydrophobic silicas have both been used in solvent-based coating formulations on a commercial scale, their use in aqueous formulations have been plagued with disadvantages. For example, in aqueous systems, either the silica additive must be increased to unacceptable levels or the formulation does not attain the desired level of performance. A demand, therefore, exists for aqueous systems which perform comparably to solvent based systems and, accordingly, for improved additives or methods to accomplish such results.

It is therefore an object of the present invention to provide a versatile and efficient rheological additive for waterborne systems, such as in coatings and other industrial applications. A further object is to provide an additive that fosters stability in aqueous compositions. A still further object is to provide a thixotrope which alleviates many of the waterborne coating rheology control formulating difficulties that exist with other inorganic and organic materials .

SUMMARY OF THE INVENTION

Accordingly, the present invention is directed to an aqueous dispersion of fumed silica that provides enhanced rheology control and thixotropy to waterborne systems. The fumed silica dispersion is uniformly dispersed in the waterborne system such that an amount ranging between 0.5 % and 10.0%, by weight, of silica is present in the final composition. The waterborne system, therefore, includes an aqueous dispersion of fumed silica, and a waterborne resin. The resin is selected from the group consisting of alkyd, acrylic, polyester, polyether, silicate, urethane, epoxy, formaldehyde, vinyl, and mixtures thereof. The fumed silica has a surface area between about 85 m²/g and about 410 m²/g.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph of the rheological performance of an epoxy resin system incorporating the present fumed silica dispersion;

FIG. 2 is a graph of the rheological performance of an bisphenol-A epoxy resin system
5 incorporating the present fumed silica dispersion;

FIG. 3 is a graph of the rheological performance of an epichlorohydrin and bisphenol-A resin system incorporating the present fumed silica dispersion;

FIG. 4 is a graph of the rheological performance of a urethane modified epoxy resin system incorporating the present fumed silica dispersion; and

10 FIG. 5 is a graph of the rheological performance of an acrylic resin system incorporating the present fumed silica dispersion; and

FIG. 6 is a graph of the response of the present fumed silica dispersion in a typical water reducing alkyd coating formulation.

DETAILED DESCRIPTION OF THE INVENTION

15 The present invention is directed to an aqueous dispersion of hydrophilic fumed silica which provides enhanced rheology control and thixotropy to aqueous or waterborne systems. The present aqueous dispersion of fumed silica is effective in alkyd, acrylic, polyester, polyether, silicate, urethane, epoxy, formaldehyde, vinyl, and mixtures or modifications thereof as vehicle systems. It has been found that unlike other organic and inorganic materials used as thixotropes
20 in waterborne systems such as coatings, the present aqueous dispersion of fumed silica will not typically react with additives in the formulation to produce unexpected side effects after product manufacture.

Fumed silicas useful in this invention are generally characterized by a chain-like structure having high surface area per unit weight. The production of fumed silica is a well-documented
25 process which involves the hydrolysis of silicon tetrachloride vapor in a flame of hydrogen and oxygen. Molten particles of roughly spherical shapes are formed in the combustion process, the diameters of which are varied through process parameters. These molten spheres of fumed silica, typically referred to as primary particles, fuse with one another by undergoing collisions at their contact points to form branched, three dimensional chain-like aggregates. The force necessary

to break aggregates is considerable and often considered irreversible because of the fusion. During cooling and collecting, the aggregates undergo further collision that may result in some mechanical entanglement to form agglomerates. Compared to the aggregates where the primary particles are fused together, agglomerates are thought to be loosely held together by Van der
5 Waals forces and can be reversed, i.e. de-agglomerated, by proper dispersion in suitable media.

The size of the primary spherical particles that comprise the fumed silica aggregates determine the surface area. The surface area of the fumed silica, as measured by the nitrogen adsorption method of S. Brunauer, P. H. Emmet, and I. Teller, J. Am. Chemical Society, Volume 60, Page 309 (1938) and commonly referred to as BET, typically ranges from about 85 m²/g to
10 about 410 m²/g. In the present invention, the fumed silica is preferably in a range from about 175 m²/g to about 225 m²/g, and are of a high purity. High purity means that the total impurity content is typically less than 1 % and preferably less than 0.01 % (i.e., 100 ppm). Although many commercially available fumed silicas are suitable, CAB-O-SIL® fumed silica, available from the Cab-O-Sil Division of Cabot Corporation, Tuscola, IL, having a surface area of about 200 m²/g
15 is most preferred. Such a silica has been found to be of high quality and is readily dispersible.

The fumed silica of the present invention is uniformly dispersed in a stable aqueous medium (e.g. deionized water) using conventional methods known to those skilled in the art. By uniformly dispersed is meant that the aggregates are isolated and well distributed throughout the medium. By stable is typically meant that the aggregates will not re-agglomerate and settle out
20 (e.g. form a hard, dense sediment). The fumed silica dispersion should have a pH between 5.0 and 10.5 and may be adjusted by the addition of a suitable base such as sodium hydroxide, potassium hydroxide, ammonia and the like. Preferably, the fumed silica dispersion of the present invention has a pH ranging between 7.0 and 9.5. The fumed silica dispersion of the present invention is preferably prepared by the method described by Miller et al., in U.S. Patent
25 No. 5,246,624, the disclosure of which is incorporated herein in its entirety by reference. Although many commercially available fumed silica dispersions are suitable, CAB-O-SPERSE® aqueous fumed silica dispersions, available from the Cab-O-Sil Division of Cabot Corporation, Tuscola, IL, are most preferred.

The waterborne systems of the present invention are prepared by combining or mixing the
30 aqueous dispersions of fumed silica directly with a waterborne resin, such as an alkyd, acrylic,

polyester, silicate, urethane, epoxy, and the like, or with a formulation containing a waterborne resin under low shear conditions (i.e., to prevent foaming) until a uniform homogeneous composition is obtained. Typically, the fumed silica dispersions range from about 10% to about 45% solids, by weight; and, preferably, between 15% and 30% solids, by weight. Most preferably, a fumed silica dispersion of about 20% solids, by weight, has been found to maximize the loading level of silica while maintaining the colloidal stability of the dispersion.

The aqueous dispersions of fumed silica of the present invention are useful in aqueous systems to provide effective rheological control (i.e., viscosity and thixotropy) for example, in industrial and automotive coating, adhesive, paint, and ink applications. It has been found that another advantage of using an aqueous dispersion of fumed silica in waterborne resin systems is to provide rheology and sag control, and anti-settling. It is also believed that a stable matrix is formed in waterborne formulations after the incorporation of the fumed silica dispersion due to electrostatic interaction. During the high-shear processes usually found in product application, the matrix disintegrates, thereby reducing viscosity and permitting near-Newtonian flow. After application, the inorganic matrix reforms at a predictable rate to provide resistance to sagging and edge-pull during film coalescence and/or cure. This matrix remains unmodified through the many physical film changes during conversion from liquid to solid, thus providing a predictable application consistency.

The aqueous dispersion of fumed silica has been found to be an effective suspension agent in some formulations due to its internally-generated structure. The product forms a matrix capable of stopping or significantly retarding undesirable striation and pigment settling, even in products containing powdered zinc or other unusually heavy pigments. It is noted that the addition of dry hydrophilic fumed silica to waterborne systems has been found to be ineffective as a rheology control agent. In particular, the viscosity of the system will tend to continually increase over time, thereby not achieving stability. In addition, the dry silica is difficult to handle and disperse, and may tend to settle out at higher loading levels.

Other advantages of the present dispersions are that they will not migrate in wet or dry films and are unaffected by heat and atmospheric exposure in the dried/cured film. The dispersion is inherently non-yellowing and will not contribute to color changes or drift in either

the wet or dry state. Moreover, the present aqueous dispersions of fumed silica are biologically inactive and is not expected support microbial activity.

The present aqueous dispersions of fumed silica used as aqueous thixotropes in water based systems are responsive to changes in pH, but have been found to be effective in the 7.0 to 9.5 pH range commonly used in products formulated for industrial and commercial use. The present dispersions have also been found to be effective in higher pH ranges, depending specifically upon the individual formulation.

Although the loading level, as a percent of total or resin solids, the precise method of incorporation, and the stage of manufacture at which this is accomplished, all play a significant role in the final effectiveness of the dispersion, the aqueous dispersion of fumed silica of the present invention has been shown to be effective in many systems used in formulating waterborne products.

The present invention will be further illustrated by the following examples, which are intended to be illustrative in nature and are not to be considered as limiting the scope of the invention.

EXAMPLE I

An aqueous colloidal dispersion of fumed silica, which can be used as an aqueous thixotrope in the present invention, was prepared and evaluated as follows.

Approximately 205.24 grams of deionized water and 0.4 gram of 38% hydrochloric acid were added to a commercial Waring blender. While mixing, 80 grams of CAB-O-SIL® PTG grade fumed silica were added to the blender. When the addition was complete, the mixture was stirred at a high rate for about five minutes. After the stirring was completed, about 108.52 grams of water were added to the mixture followed by about 6.12 grams of a 10% potassium hydroxide solution stabilizer. After the addition of the stabilizer, the mixture was stirred for an additional two minutes. The aqueous fumed silica dispersion prepared had a 20% solids level, a viscosity of about 65 centipoise, and a pH of 9.

EXAMPLE II

A scaled-up volume of the dispersion of EXAMPLE I was prepared, using 2-amino-2-methyl-1-propanol, available as AMP-95™ from Angus Chemical Company, Buffalo Grove, IL, as the base-stabilizer. Approximately 1283.80 grams of water were mixed with 0.251 gram of
5 38% hydrochloric acid. About 499.92 grams of CAB-O-SIL® PTG grade fumed silica were then added to the water/acid mixture, and was stirred for about 20 minutes. 678 grams of deionized water was then added to the mixture, followed by 10.54 grams of the AMP-95™ stabilizer. The aqueous fumed silica dispersion prepared had a 20.22% solids level, and a pH of 9.

EXAMPLE III

10 A waterborne system, including an aqueous fumed silica dispersion (similar to the dispersion prepared in EXAMPLE I) and a waterborne epoxy resin, was prepared and evaluated to determine the effectiveness of the present dispersion as a thixotrope for waterborne systems. The aqueous fumed silica dispersion was mixed with Waterpoxy® 701 Resin epoxy curing agent, available from Henkel Corporation, Ambler, PA, until a loading level of 2% dry silica on resin
15 solids was achieved. The viscosity (centipoise), shear thinning index (STI), and pH were then measured after sample preparation (0 days), and after periods of 1 and 7 days. The viscosity was measured on a Brookfield viscometer using Nos. 3 or 4 spindle at 6 and 60 RPM's. The experimental results are presented below in Table 1.

TABLE 1

| | | | | |
|----|------------------|------|------|------|
| 20 | DAYS | 0 | 1 | 7 |
| | VISCOSITY | | | |
| | Sample 1, 6 RPM | 1500 | 1500 | 1500 |
| | Sample 1, 60 RPM | 1442 | 1442 | 1442 |
| | Sample 2, 6 RPM | 3300 | 3900 | 3800 |
| 25 | Sample 2, 60 RPM | 1990 | 2540 | 2590 |

| | | | | |
|---|----------|-------|-------|-------|
| | STI | | | |
| | Sample 1 | 1.04 | 1.04 | 1.04 |
| | Sample 2 | 1.66 | 1.53 | 1.51 |
| | pH | | | |
| 5 | Sample 1 | 11.33 | 11.33 | 11.33 |
| | Sample 2 | 11.29 | 11.41 | 10.99 |

FIG. 1 is a graph of the viscosity of a control sample (Sample 1), a waterborne epoxy resin without a rheology control agent, versus the present waterborne system (Sample 2) over time. Both Table 1 and FIG. 1 illustrate that the present waterborne system achieved stable performance after about 1 day and a desired increase in viscosity.

EXAMPLE IV

A waterborne system, including an aqueous fumed silica dispersion (similar to the dispersion prepared in EXAMPLE I) and a waterborne bisphenol-A epoxy resin, was prepared and evaluated to determine the effectiveness of the present dispersion as a thixotrope for waterborne systems. The aqueous fumed silica dispersion was mixed with EPI-REZ® 3510-W-60 nonionic, aqueous dispersion of bisphenol-A epoxy resin, available from Shell Chemical Co., Houston, TX, until a loading level of 2% dry silica on resin solids was achieved. The viscosity (centipoise), shear thinning index (STI), and pH were then measured after sample preparation (0 days), and after periods of 1 and 7 days. The viscosity was measured on a Brookfield viscometer using Nos. 3 or 4 spindle at 6 and 60 RPM's. The experimental results are presented below in Table 2.

TABLE 2

| DAYS | 0 | 1 | 7 |
|-----------|---|---|---|
| VISCOSITY | | | |

| | | | | |
|----|------------------|------|------|------|
| | Sample 1, 6 RPM | 220 | 220 | 220 |
| | Sample 1, 60 RPM | 178 | 178 | 178 |
| | Sample 2, 6 RPM | 520 | 500 | 400 |
| | Sample 2, 60 RPM | 264 | 270 | 260 |
| 5 | STI | | | |
| | Sample 1 | 1.24 | 1.24 | 1.24 |
| | Sample 2 | 1.97 | 1.85 | 1.85 |
| | pH | | | |
| | Sample 1 | 3.41 | 3.41 | 3.41 |
| 10 | Sample 2 | 5.70 | 7.04 | 7.04 |

FIG. 2 is a graph of the viscosity of a control sample (Sample 1), a waterborne bisphenol-A epoxy resin without a rheology control agent, versus the present waterborne system (Sample 2) over time. Both Table 2 and FIG. 2 illustrate that the present waterborne system achieved stable performance, particularly the Sample 2 measured at 60 RPM, and a desired increase in viscosity. The Sample 2 viscosity measured at 6 RPM decreased more rapidly.

EXAMPLE V

A waterborne system, including an aqueous fumed silica dispersion (similar to the dispersion prepared in EXAMPLE I) and a waterborne epichlorohydrin and bisphenol-A epoxy resin, was prepared and evaluated to determine the effectiveness of the present dispersion as a thixotrope for waterborne systems. The aqueous fumed silica dispersion was mixed with EPI-REZ® 3510-WY-55 (55% solids) dispersion of Econ™ 1001F condensation product of epichlorohydrin and bisphenol-A in water, available from Shell Chemical Co., Houston, TX, until a loading level of 2% dry silica on resin solids was achieved. The viscosity (centipoise), shear thinning index (STI), and pH were then measured after sample preparation (0 days), and after

periods of 1 and 7 days. The viscosity was measured on a Brookfield viscometer using Nos. 3 or 4 spindle at 6 and 60 RPM's. The experimental results are presented below in Table 3.

TABLE 3

| | | | | |
|----|------------------|------|------|-------|
| | DAYS | 0 | 1 | 7 |
| 5 | VISCOSITY | | | |
| | Sample 1, 6 RPM | 2700 | 2700 | 2700 |
| | Sample 1, 60 RPM | 1010 | 1010 | 1010 |
| | Sample 2, 6 RPM | 3000 | 5600 | 15400 |
| | Sample 2, 60 RPM | 1130 | 1950 | 3700 |
| 10 | STI | | | |
| | Sample 1 | 2.67 | 2.67 | 2.67 |
| | Sample 2 | 2.65 | 2.87 | 4.16 |
| | pH | | | |
| | Sample 1 | 8.74 | 8.74 | 8.74 |
| 15 | Sample 2 | 9.38 | 9.36 | 7.40 |

FIG. 3 is a graph of the viscosity of a control sample (Sample 1), a waterborne epichlorohydrin and bisphenol-A epoxy resin without a rheology control agent, versus the present waterborne system (Sample 2) over time. Both Table 3 and FIG. 3 illustrate that the present waterborne system achieved a desired increase in viscosity while providing semi-stable performance in thixotropy. The Sample 2 viscosity measured 6 RPM increased rapidly. The Sample 2 measured at 60 RPM increased less rapidly and was more stable.

EXAMPLE VI

A waterborne system, including an aqueous fumed silica dispersion (similar to the dispersion prepared in EXAMPLE I) and a waterborne urethane modified epoxy resin, was prepared and evaluated to determine the effectiveness of the present dispersion as a thixotrope for waterborne systems. The aqueous fumed silica dispersion was mixed with EPI-REZ® 5520-W-60 nonionic aqueous dispersion of urethane modified epoxy resin, available from Shell Chemical Co., Houston, TX, until a loading level of 2% dry silica on resin solids was achieved. The viscosity (centipoise), shear thinning index (STI), and pH were then measured after sample preparation (0 days), and after periods of 1 and 7 days. The viscosity was measured on a Brookfield viscometer using Nos. 3 or 4 spindle at 6 and 60 RPM's. The experimental results are presented below in Table 4.

TABLE 4

| DAYS | 0 | 1 | 7 |
|------------------|-------|-------|-------|
| VISCOSITY | | | |
| Sample 1, 6 RPM | 5600 | 5600 | 5600 |
| Sample 1, 60 RPM | 1440 | 1440 | 1440 |
| Sample 2, 6 RPM | 29450 | 17200 | 17900 |
| Sample 2, 60 RPM | 3710 | 2730 | 2920 |
| STI | | | |
| Sample 1 | 3.89 | 3.89 | 3.89 |
| Sample 2 | 7.94 | 6.30 | 6.13 |
| pH | | | |
| Sample 1 | 3.51 | 3.51 | 3.51 |
| Sample 2 | 7.37 | 7.53 | 7.40 |

FIG. 4 is a graph of the viscosity of a control sample (Sample 1), a waterborne urethane modified epoxy resin without a rheology control agent, versus the present waterborne system (Sample 2) over time. Both Table 4 and FIG. 4 illustrate that the present waterborne system achieved stable performance after about 1 day and a desired increase in viscosity.

5

EXAMPLE VII

A waterborne system, including an aqueous fumed silica dispersion (similar to the dispersion prepared in EXAMPLE I) and a waterborne acrylic copolymer resin, was prepared and evaluated to determine the effectiveness of the present dispersion as a thixotrope for waterborne systems. The aqueous fumed silica dispersion was mixed with Neocryl® A-639 waterborne acrylic copolymer, available from Zeneca Resins, Wilmington, MA, until a loading level of 2% dry silica on resin solids was achieved. The viscosity (centipoise), shear thinning index (STI), and pH were then measured after sample preparation (0 days), and after periods of 1 and 7 days. The viscosity was measured on a Brookfield viscometer using Nos. 3 or 4 spindle at 6 and 60 RPM's. The experimental results are presented below in Table 5.

15

TABLE 5

20

| DAYS | 0 | 1 | 7 |
|------------------|------|------|------|
| VISCOSITY | | | |
| Sample 1, 6 RPM | 480 | 480 | 480 |
| Sample 1, 60 RPM | 212 | 212 | 212 |
| Sample 2, 6 RPM | 540 | 680 | 580 |
| Sample 2, 60 RPM | 254 | 282 | 258 |
| STI | | | |
| Sample 1 | 2.26 | 2.26 | 2.26 |
| Sample 2 | 2.13 | 2.41 | 2.25 |

| pH | | | |
|----------|------|------|------|
| Sample 1 | 6.53 | 6.53 | 6.53 |
| Sample 2 | 6.59 | 6.49 | 6.53 |

FIG. 5 is a graph of the viscosity of a control sample (Sample 1), a waterborne urethane modified epoxy resin without a rheology control agent, versus the present waterborne system (Sample 2) over time. Both Table 5 and FIG. 5 illustrate that the present waterborne system achieved stable performance after about 1 day and desired increase in viscosity.

EXAMPLE VIII

A coating formulation, incorporating the aqueous fumed silica dispersion of the present invention, a waterborne acrylic resin system, and various additives, was prepared and evaluated to determine the effectiveness of the present dispersion as a thixotrope in coatings. A high gloss waterborne topcoat, based on Neocryl® XK90 acrylic copolymer emulsion, available from Zeneca Resins, Wilmington, MA, was prepared. The coating formulation, as set forth below in Table 6, was prepared by first mixing the components of Part A in a Waring Blender at high speed for about 5 minutes. The Part B components were then added and dispersed into the Part A mixture in the Waring Blender at high speed for about 5 minutes. The viscosity (mPas), STI, and pH were then measured after periods of 2 days, 25 days, and 60 days. These measurements were taken for a high gloss aqueous top coat formulation without any commercial thickening agent (Control), and a similar formulation utilizing an aqueous fumed silica dispersion (similar to the dispersion prepared in Example I) as an aqueous thixotrope (Sample). The viscosity of the coatings was measured on a Brookfield Rotary Viscometer RVD-II using spindle Nos. 1 or 2 at speeds of 0.5, 1.0, 2.5, 5.0, and 10.0 RPM. The STI is a ratio of the measured viscosity at 0.5 and 5.0 RPM's. The experimental results are presented below in Table 7.

TABLE 6

| FORMULATION | CONTROL (WT. %) | SAMPLE (WT. %) |
|-------------|--------------------|-------------------|
|-------------|--------------------|-------------------|

| | | | |
|----|---|--------|--------|
| | Part A: | | |
| | Deionized water | 4.96 | 0.94 |
| | Neocryl® XK90 acrylic dispersion | 23.65 | 23.56 |
| 5 | Dehydran™ 1293 defoamer (Henkel) | 0.30 | 0.30 |
| | Disperse™ Ayd W22 dispersant (Daniel) | 0.34 | 0.34 |
| 10 | Aqueous Fumed Silica Dispersion (i.e., Example I) | -- | 5.00 |
| | Butyl Glycol-coalescent | 1.78 | 1.77 |
| | TiO ₂ | 18.78 | 18.78 |
| | Part B: | | |
| | Butyl Glycol | 1.78 | 1.78 |
| 15 | Neocryl®XK90 | 48.0 | 47.10 |
| | NaNO ₂ , 30% sol'n.-rust inhibitor | 0.41 | 0.41 |
| | | 100.00 | 100.00 |

TABLE 7

| | | | | |
|----|------------------|------|------|------|
| | DAYS | 2 | 25 | 60 |
| 20 | VISCOSITY (mPas) | | | |
| | Control, 0.5 RPM | 100 | 90 | 70 |
| | 1.0 RPM | 90 | 60 | 70 |
| | 2.5 RPM | 72 | 58 | 56 |
| 25 | 5.0 RPM | 66 | 54 | 56 |
| | 10.0 RPM | 60 | 52 | 55 |
| | Sample, 0.5 RPM | 2560 | 1280 | 1280 |
| | 1.0 RPM | 1720 | 1040 | 1080 |

| | | | | |
|---|------------------|------|------|------|
| | 2.5 RPM | 1010 | 752 | 784 |
| | 5.0 RPM | 720 | 620 | 648 |
| | 10.0 RPM | 524 | 508 | 536 |
| 5 | STI (0.5/5.0RPM) | | | |
| | Control | 1.52 | 1.66 | 1.25 |
| | Sample | 3.56 | 2.06 | 1.98 |

As illustrated above, the aqueous dispersion of the present invention can be incorporated not only in resins but also in coating formulations.

10

EXAMPLE IX

A coating formulation, incorporating the aqueous fumed silica dispersion of the present invention, a waterborne alkyd resin system, and various additives, was prepared and evaluated to determine the effectiveness of the present dispersion as a thixotrope in coatings. An aqueous industrial maintenance coating based on Resydrol® AY 466 W, 38%, alkyd resin emulsion, available from Hoechst Celanese, Fine Chemicals Division, Charlotte, NC, was prepared. The coating formulation, as set forth below in Table 8, was prepared by mixing the components in a Waring blender at high speed for about 5 minutes. The viscosity (mPas) and STI were then measured after periods of 1, 18 and 60 days. These measurements were taken for an aqueous industrial maintenance coating of formulation with and without a commercial thickening agent (Borchigel™ L75N, 54%), and a similar formulation utilizing an aqueous fumed silica dispersion (similar to the dispersion prepared in Example I) as an aqueous thixotrope (Sample). The viscosity of the coatings was measured on a Brookfield Rotary Viscometer. The experimental results are presented below in Table 9. FIG. 6 is a graph illustrating the viscosity aging over time, taken from the data in Table 9, and corresponding to a shear rate of 1.4 dynes/sec. At a finess of grind <10 microns (the graph was converted from mPas to centipoise). As illustrated in FIG. 6, the aqueous fumed silica dispersion achieved and maintained a stable workable viscosity for an extended period of time. The Control sample exhibited a high initial increase in viscosity and substantial loss over time.

TABLE 8

| | FORMULATION | CONTROL (WT. %) | SAMPLE (WT. %) |
|----|---|--------------------|-------------------|
| | Resydrol®AY466 W,38% | 70.00 | 69.02 |
| | Aqueous Ammonia, 10% | 3.00 | 2.96 |
| 5 | Additol™ VXW 4940 drying agent (Hoechst Celanese) | 1.30 | 1.28 |
| | Titanox™ 2300 (Kronos) | 21.24 | 20.94 |
| | Borchigel™ L7SN, 54% thickener | 1.86 | -- |
| 10 | Aqueous Fumed Silica Dispersion (i.e., Example I) | -- | 4.81 |
| | Additol™ VXW 4973 defoamer | 0.30 | 0.30 |
| | Surfynol™ SE-F wetting agent (Air Products) | 0.30 | 0.30 |
| 15 | Additol™ XL 297 antiskinning agent | 0.40 | 0.39 |
| | Deionized water | 1.60 | -- |
| | | 100.00 | 100.00 |

TABLE 9

| | DAYS | 1 | 18 | 60 |
|----|--------------------------------------|-------|-------|-------|
| 20 | VISCOSITY | | | |
| | Control | 6.660 | 4.340 | 3.472 |
| | Control without Borchigel™ thickener | 0.785 | 0.588 | 0.588 |
| 25 | Sample | 1.985 | 2.940 | 3.087 |
| | STI | | | |

| | | | |
|---------------------------|------|------|------|
| Control | 1.54 | 1.27 | 1.66 |
| Control without thickener | 3.13 | 1.81 | 1.88 |
| Sample | 3.33 | 4.64 | 2.63 |

- 5 As illustrated above, the aqueous dispersion of the present invention can be incorporated not only in resins but also in coating formulations.

Although particular embodiments of the invention have been described in detail for purposes of illustration, various changes and modifications may be made without departing from the scope and spirit of the invention. Accordingly, the invention is not to be limited except as
10 by the appended claims.

What is claimed is:

CLAIMS

1. A waterborne system, comprising:
an aqueous dispersion of fumed silica; and
a waterborne resin;
5 wherein said fumed silica has a surface area between about 85 m²/g and about 410 m²/g.
2. The waterborne system of claim 1, wherein said fumed silica has a surface area between about 175 m²/g and about 225 m²/g.
3. The waterborne system of claim 2, wherein said fumed silica has a surface area of
10 about 200 m²/g.
4. The waterborne system of claim 1, wherein said fumed silica has an impurity level of less than 1%.
5. The waterborne system of claim 1, wherein said system comprises between about 0.5 and about 10.0% fumed silica, by weight, of total resin solids.
- 15 6. The waterborne system of claim 5, wherein said system comprises between about 0.5 and about 5.0% fumed silica, by weight, of total resin solids.
7. The waterborne system of claim 6, wherein said system comprises about 2.0% fumed silica, by weight, of total resin solids.
8. The waterborne system of claim 1, wherein said aqueous dispersion of fumed silica
20 has between 10% and 45%, by weight, silica solids.
9. The waterborne system of claim 8, wherein said aqueous dispersion of fumed silica has between 15% and 30%, by weight, silica solids.

10. The waterborne system of claim 9, wherein said aqueous dispersion of fumed silica has 20%, by weight, silica solids.
11. The waterborne system of claim 1, wherein said aqueous dispersion of fumed silica has a pH between about 5.0 and about 10.5.
- 5 12. The waterborne system of claim 11, wherein said aqueous dispersion of fumed silica has a pH between about 7.0 and about 9.5.
13. The waterborne system of claim 1, further comprising at least one additive selected from the group consisting of surfactants, coalescing solvents, pigments, defoamers, antiskinning agents, drying agents, wetting agents, thickening agents, dispersing agents, 10 biocides, and corrosion inhibitors.
14. The waterborne system of claim 1, wherein said waterborne resin is selected from the group consisting of alkyd, acrylic, polyester, polyether, silicate, urethane, epoxy, formaldehyde, vinyl, and mixtures thereof.

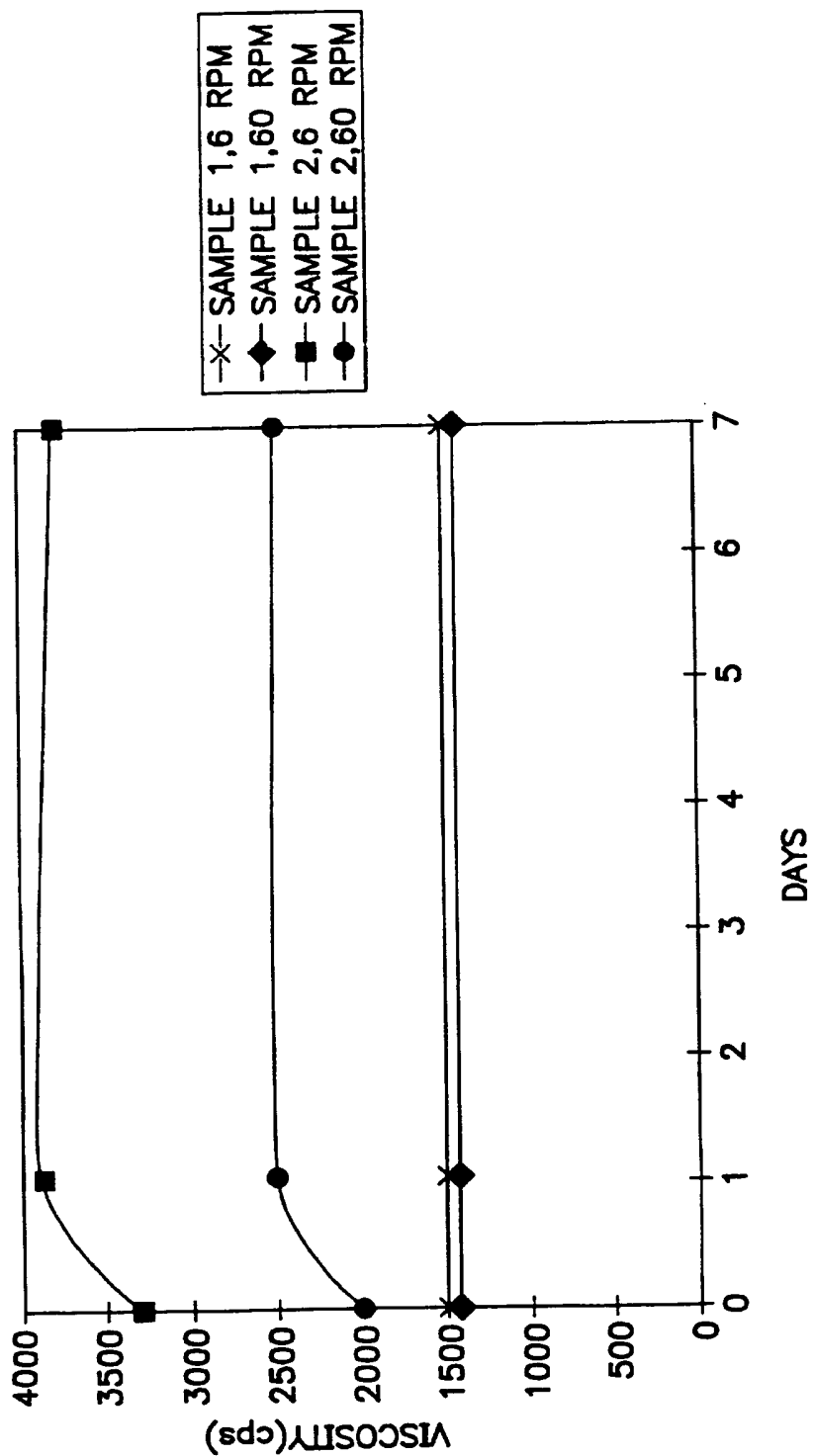


FIG. 1

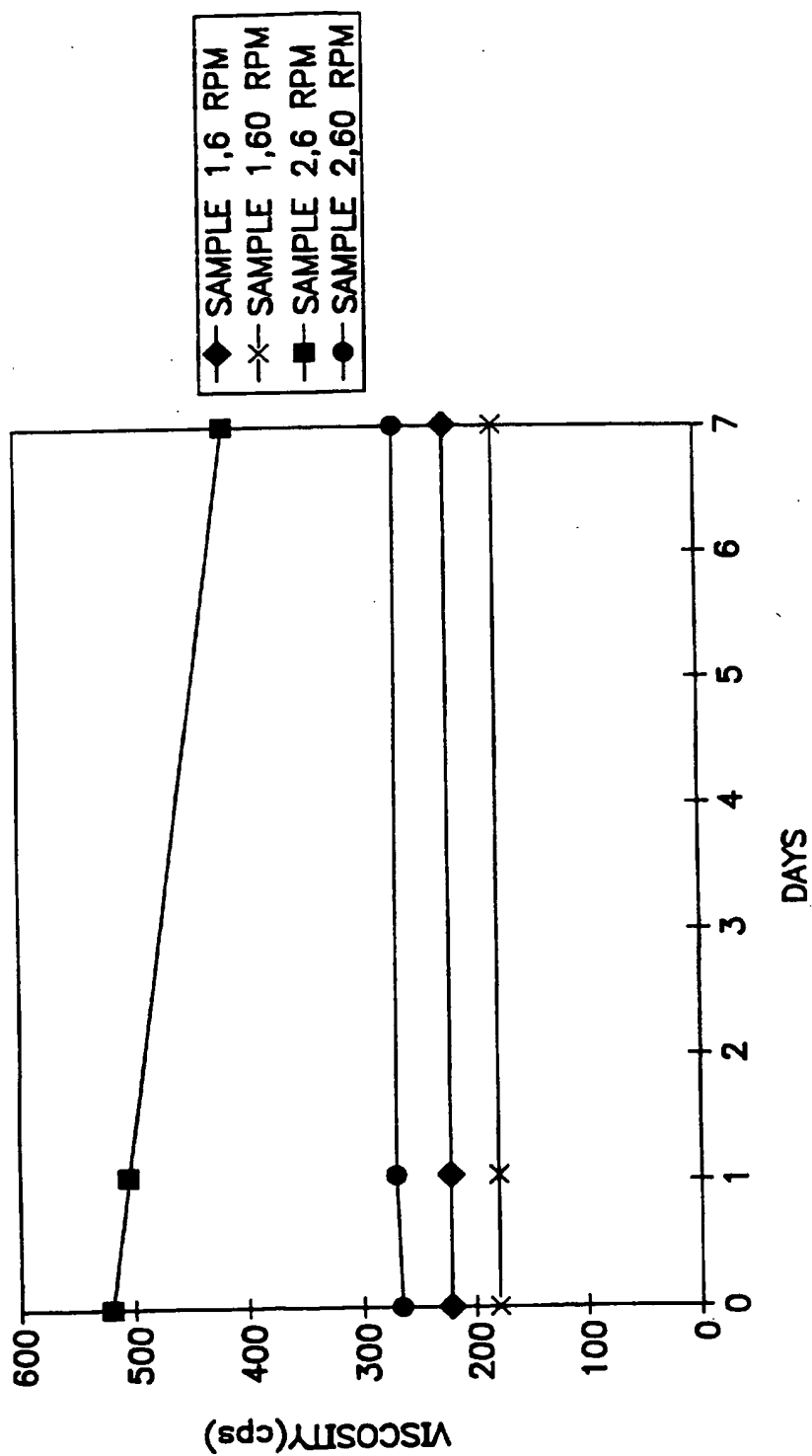


FIG. 2

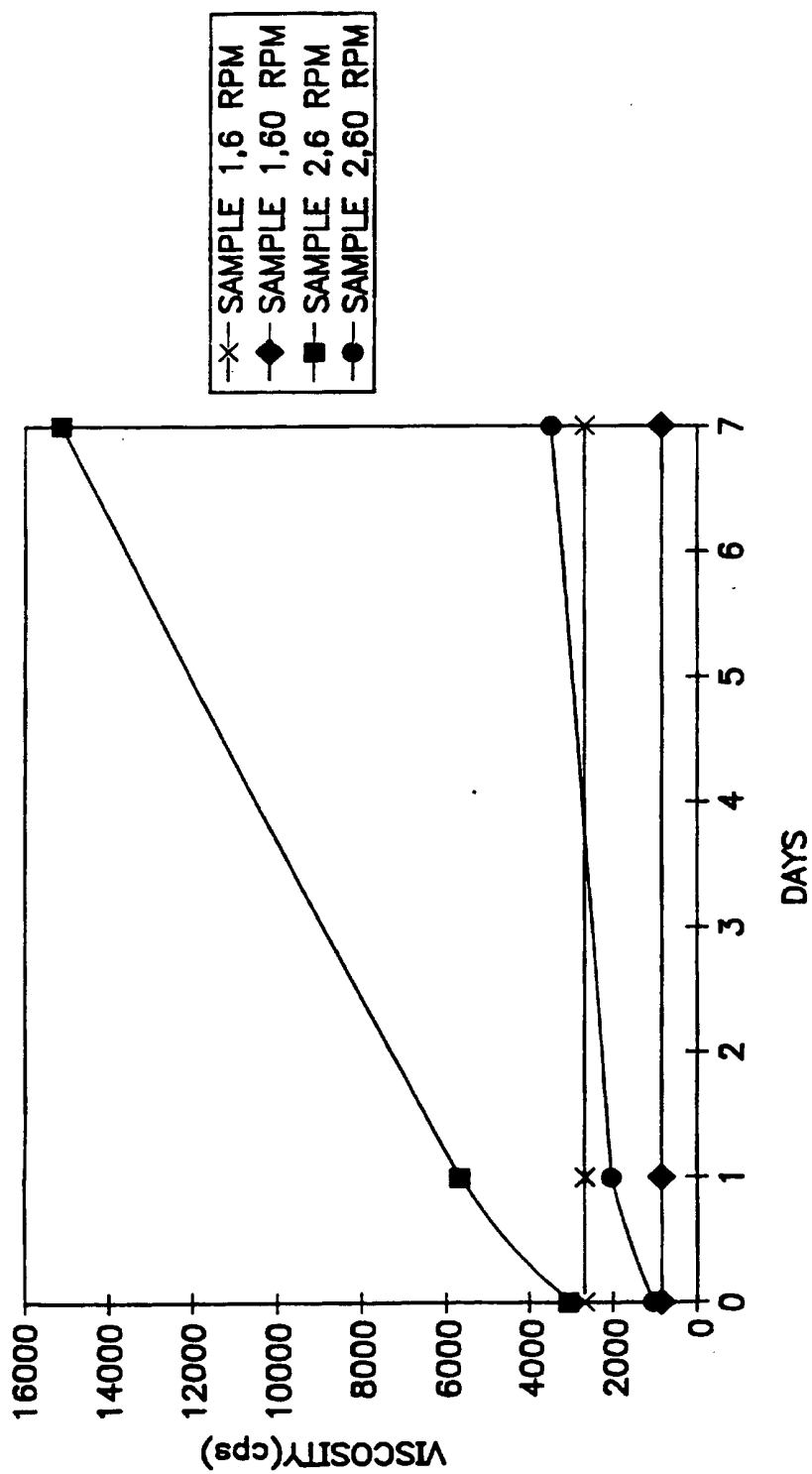


FIG. 3

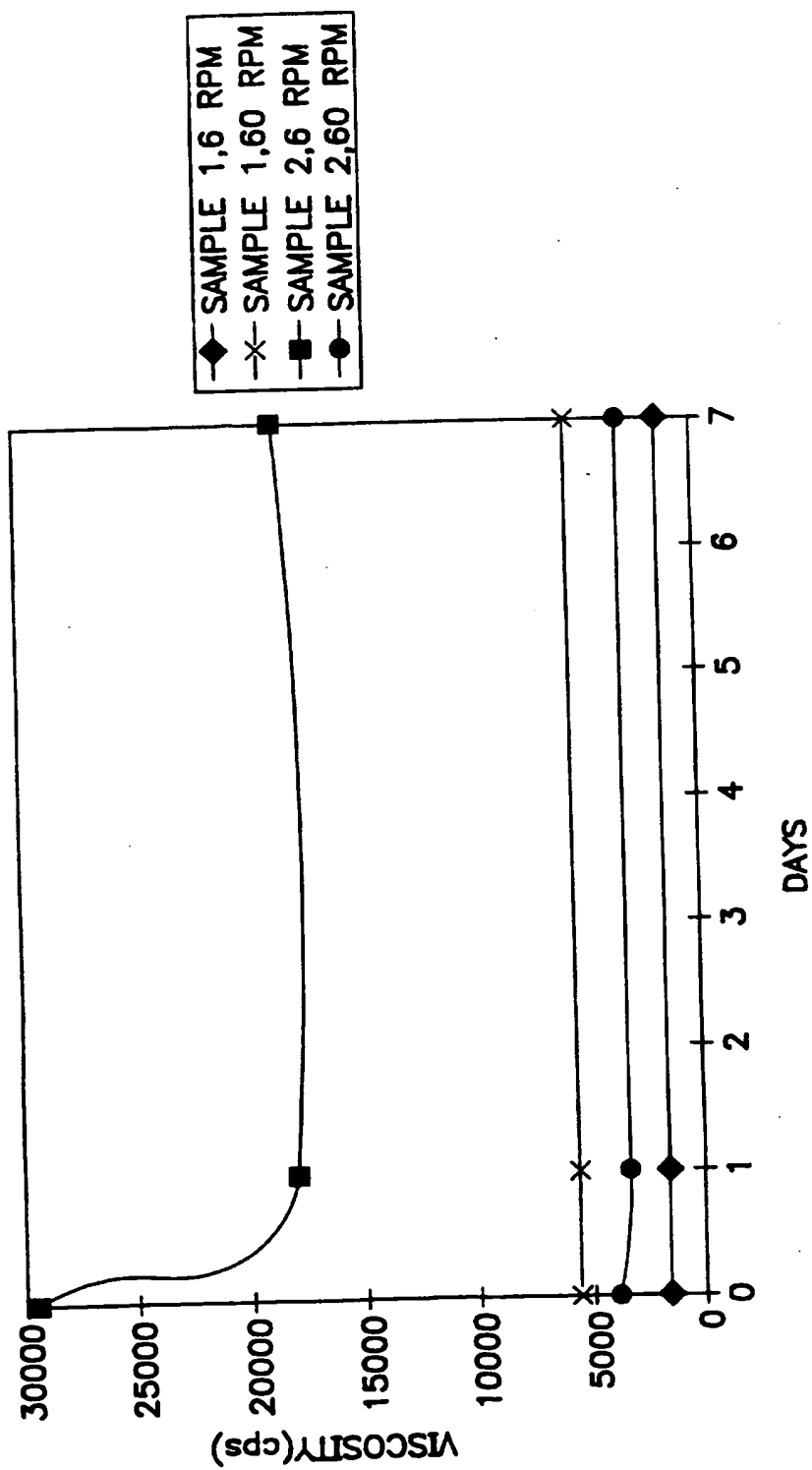


FIG. 4

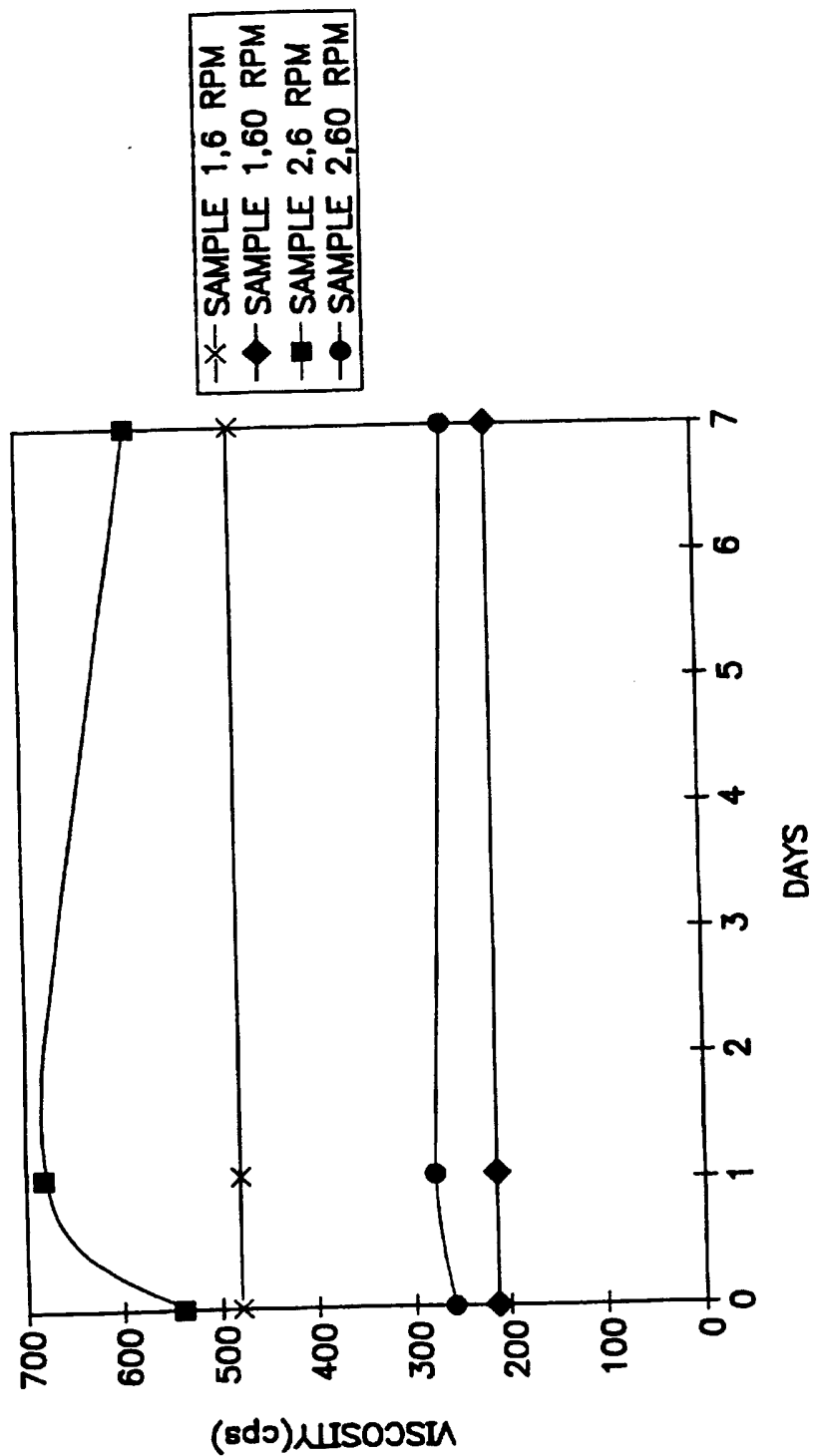


FIG. 5

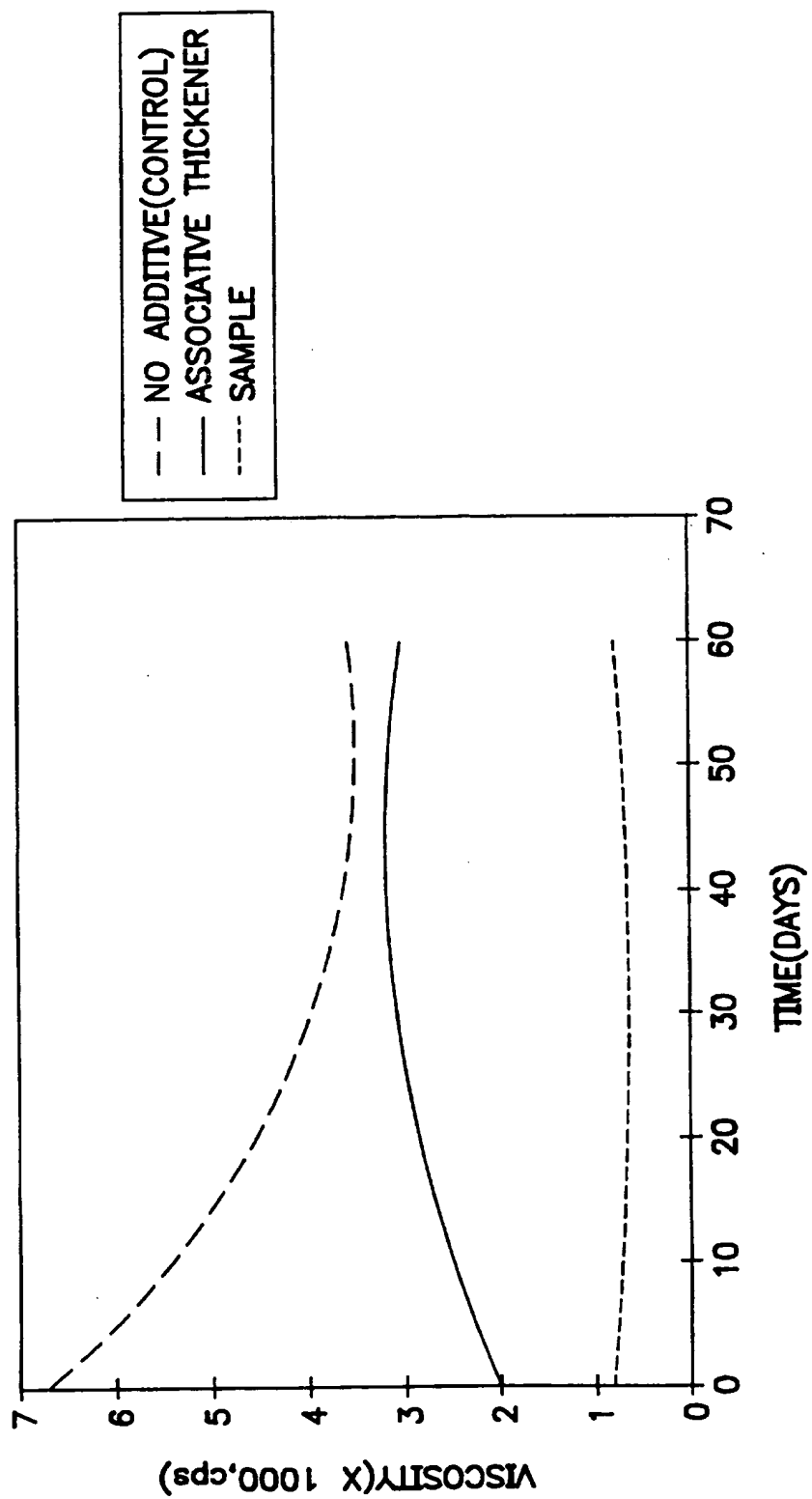


FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/15940

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D5/04 C09D7/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | EP 0 399 442 A (BASF CORPORATION) 28 November 1990 see abstract see page 2, line 48-52 see page 3, line 1-5 see page 4, paragraph 3 --- | 1-4, 13, 14 |
| A | WO 94 18277 A (CABOT CORPORATION) 18 August 1994 see abstract see claim 2 --- | 1 |
| A | US 4 455 331 A (ROBERT J. BARSOTTI) 19 June 1984 see claims 1-3 ----- | |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- * "O" document referring to an oral disclosure, use, exhibition or other means
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* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

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11.02.97

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/15940

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| EP-A-399442 | 28-11-90 | AT-T- 110095 | 15-09-94 |
| | | DE-D- 69011580 | 22-09-94 |
| | | DE-T- 69011580 | 18-05-95 |
| | | ES-T- 2062167 | 16-12-94 |
| ----- | | | |
| WO-A-9418277 | 18-08-94 | AU-B- 673583 | 14-11-96 |
| | | AU-A- 6160494 | 29-08-94 |
| | | BR-A- 9405723 | 28-11-95 |
| | | CA-A- 2155407 | 18-08-94 |
| | | CN-A- 1118605 | 13-03-96 |
| | | EP-A- 0683809 | 29-11-95 |
| | | JP-T- 8506611 | 16-07-96 |
| | | US-A- 5472493 | 05-12-95 |
| ----- | | | |
| US-A-4455331 | 19-06-84 | BE-A- 897419 | 30-01-84 |
| | | CA-A- 1213689 | 04-11-86 |
| ----- | | | |

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